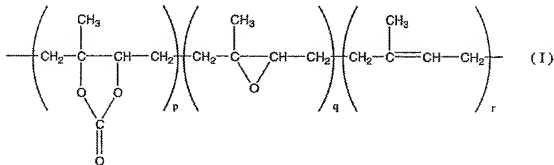**REMARKS**

Applicant has amended claims 1-3 and 6-8. The claim language is supported by the as-filed specification, *e.g.*, page 8, lines 22-24. No new matter has been introduced. A revised drawing of the formula (I) in claim 1 is included as suggested at page 2 of the Office Action.

Applicant respectfully requests reconsideration and withdrawal of the 35 U.S.C. §§ 102(b) and 103(a) rejection of claim 1 over SU 422262 ("SU '262"). Applicant also respectfully traverses the § 103(a) rejection of claims 1-8 over SU '262 in view of JP 2002-053573 ("JP '573"), and the § 103(a) rejection of claims 1-8 over SU '262 in view of Kawanami et al., *Research of carbonate synthesis using supercritical carbon dioxide and ionic liquid*, Abstracts of Presentation, the 35th Fall Meeting of Society of Chemical Engineers, Japan, September 18-20, 2002, Vol. 35, p. 391 ("Kawanami").

The Office Action asserts that claim 1 does not "exclude 1,2 and 3,4 addition units." Office Action, p. 4.

Claim 1 is amended to recite, "[a] cyclic carbonate-containing polymeric compound consisting essentially of a polymeric compound represented by formula (I):



wherein . . . the sum of p, q, and r is 1."

By this amendment, claim 1 limits the scope of the compound to consist essentially of the structure expressly depicted in the formula (I). Any other monomer units that are not included in the formula (I) and that would materially affect the basic and novel characteristics of the claimed compound are excluded from the claim. See M.P.E.P. §2111.03.

As explained in the remarks previously presented in the Reply to Office Action filed August 12, 2009 at pages 5-6, the method as taught in SU '262 would not result in the same final compound as recited in claim 1. Applicant respectfully submits that natural rubber has no amount of 1, 2 and 3, 4 addition units while synthetic polyisoprene contains these units, as evidenced by the teachings of the following documents: S. Amnuaypornsri et al., *Green Strength of Natural Rubber: The Origin of the Stress-Strain Behavior of Natural Rubber,* Journal of Applied Polymer Science, Vol. 111, pp. 2127-2133 (2009) ("Amnuaypornsri") (copy attached); Komuro et al., Treatise of Technologies for Processing Synthetic Rubbers, Isoprene Rubbers, Vol. 1, page 10 (1975) ("Komuro") (copy of relevant portions attached along with their English translation).

Amuaypornsri provides analysis of natural polyisoprene and synthetic polyisoprene. For example, Amuaypornsri discloses that "NR [(a natural rubber)] contains 100 % cis-1,4-isoprene units, whereas Kraton IR-309 [(a synthetic rubber)] has been estimated to contain about 92% cis-1,4-isoprene units," and that the remaining portions of Kraton IR-309 include 3,4-units, as shown in Figure 4. See page 2128, right column, 3rd paragraph; page 2131, right column, 2nd paragraph.

Komuro also discloses structures of repeating units, i.e., cis-1,4-unit, trans-1,4-unit, 1,2-unit, and 3,4-unit, which may be produced theoretically by polymerization of isoprene monomers in Table 2-1.

If a synthetic rubber, which contains 3,4-units, is epoxidized and then is reacted with carbon dioxide, similarly to the method in Example 2 of SU '262, extra units derived from 3,4-units will be formed. The chemical structure of the extra units derived from 3,4-units is different from that of cyclic carbonate unit, the leftmost monomer unit in the formula (I) derived from cis-1,4- units. Therefore, the extra units derived from 3,4 units, which would be produced in Example 2 of SU' 262, are not included in the structure represented by the formula (I) and would materially affect the basic and novel characteristics of the claimed compound consisting essentially of a cyclocarbonated polymeric compound represented by the formula (I) wherein the sum of p, q, and r is 1.

For at least the foregoing reasons and the reasons set forth in the previous August 12, 2009 Reply, Example 2 of SU '262 would not necessarily result in the claimed compound. Claim 1, and its dependent claims, are neither anticipated by, nor obvious over, SU '262.

Claim 2 has been amended to positively recite "deproteinizing natural rubber," which is neither disclosed nor suggested in SU' 262. One of ordinary skill in the art would not have had any reason to incorporate any "deproteinizing [of] natural rubber" into the method of SU '262. Also, neither JP '573 nor Kawanami discloses or suggests deproteinzing natural rubber. Accordingly, amended claim 2 is allowable over the cited references for this additional reason. Also, none of these references discloses or

suggest the compound expressly recited in amended claim 1, from which claim 2 depends.

In view of the foregoing amendments and remarks, Applicant respectfully requests reconsideration of this application, withdrawal of the rejections, and timely allowance of the pending claims.

Please grant any extensions of time required to enter this response and charge any additional required fees to our deposit account 06-0916.

Respectfully submitted,
FINNEGAN, HENDERSON, FARABOW,
GARRETT & DUNNER, L.L.P.

Dated: February 4, 2010    By:___/Anthony M. Gutowski/_____
Anthony M. Gutowski
Reg. No. 38,742
(202) 408-4000

**Attachments:**

(1) S. Amnuaypornsri et al., *Green Strength of Natural Rubber: The Origin of the Stress-Strain Behavior of Natural Rubber,* Journal of Applied Polymer Science, Vol. 111, pp. 2127-2133 (2009); and

(2) Relevant portions of Komuro et al., Treatise of Technologies for Processing Synthetic Rubbers, Isoprene Rubbers, Vol. 1 (1975), including an English translation.

# Green Strength of Natural Rubber: The Origin of the Stress–Strain Behavior of Natural Rubber

Sureerut Amnuaypornsri,[1] Jitladda Sakdapipanich,[1,2] Yasuyuki Tanaka[2]

[1]*Department of Chemistry and Center of Excellence for Innovation in Chemistry, Faculty of Science, Mahidol University, Bangkok 10400, Thailand*
[2]*Institute of Science and Technology for Research and Development, Mahidol University, Salaya Campus, Nakhonphatom 73170, Thailand*

**ABSTRACT:** The variation of the green strength of natural rubber (NR) with the preparation method of the film was studied to elucidate the origin of the stress–strain behavior characteristics of NR in connection with the structure of branch points in NR. A rubber film prepared via casting from NR latex showed the highest modulus and green strength in comparison with films prepared via casting from a toluene solution-and via the hot pressing of dry rubber. The modulus and green strength of the NR latex-casting film decreased after the hot-press treatment of the film. On the other hand, no difference was observed for synthetic cis-1,4-polyisoprene rubber with the preparation method of the film or the heat treatment. This stress–strain behavior characteristics of NR can be ascribed to the changes in the branch points of the NR film with the casting method, which may result in differences in entanglement and crystallizability on stretching. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 111: 2127–2133, 2009

**Key words:** film preparation; green strength; natural rubber

## INTRODUCTION

The green strength, an elastomer's resistance to deformation and fracture before vulcanization, is, like processability and tackiness, an important property of elastomers. Elastomers with an appropriate green strength are desirable for tire production so that they will not creep and hence distort excessively before molding or tear during the expansion that occurs during molding or in the second stage for radial tires. The most meaningful measure for the characteristics of the green strength is obtained by an examination of the stress–strain curves at a given rate of strain. The shape of the stress–strain curve is an important criterion for determining the green property. The green strength of elastomers has been commonly attributed to long-chain branching,[1,2] interactions between polar groups,[1] the presence of a gel,[1,3] chain entanglements,[3,4] and crystallization on

stretching.[3] The differences in these factors are responsible for the differences in the green strength for various elastomers.

Natural rubber (NR) from *Hevea brasiliensis* is known to have very high green strength in comparison with synthetic rubbers, especially synthetic cis-1,4-polyisoprene rubber (IR). This difference in the green strength has been attributed to the crystallizability derived from the regularity of isoprene units in the cis-1,4 configuration and non-rubber constituents present in NR. The former is presumed to be the reason that NR shows a very high green strength versus IR, whereas the lower green strength of Guayule rubber from *Parthenium argentatum* is believed to be due to the absence of nonrubber components characteristic of NR. One of the characteristics of NR can be seen in the crystallization at low temperatures. The rates of crystallization of NR and enzymatically deproteinized natural rubber (DPNR) at −25°C were almost the same, whereas the rate decreased significantly after the removal of free fatty acids by acetone extraction.[5] The rate was partly recovered after the removal of the linked fatty acids in the acetone-extracted sample by transesterification, and this could be ascribed to the improvement of the rubber purity.[6] The rate of crystallization of acetone-extracted NR was accelerated by the addition of 1% (w/w) methyl linoleate.[7] However, the crystallization of transesterified DPNR was suppressed by

the addition of methyl linoleate as in the case of IR[8] because of the lack of fatty acids linked to rubber molecules.[7,9] These findings demonstrate that both the outstanding green strength and high crystallizability of NR are presumably derived from the linked fatty acids, which promote crystallization on stretching and at low temperatures. Similar tendencies for NR and IR with respect to crystallization on stretching have been observed. In the case of the crystallization of cured rubber on stretching, it was reported that NR started crystallization at a strain of 270%, whereas the strain of cured IR was 330% by dilatometric measurement.[10]

NR recovered from skim latex, that is, the rubber from small rubber particles, shows low green strength comparable to that of IR.[11] The rubber from small rubber particles has been found to be a linear polymer with no fatty acid ester group linked or associated with the NR chain.[12] These findings suggest that the presence of long-chain branching in ordinary NR is the reason for the high green strength characteristic of NR. Here, it is necessary to take into consideration that most of the branch points in ordinary NR are formed by both functional terminal groups via hydrogen bonding and the association of phospholipid groups at the chain end, that is, the α terminal.[13,14] Proteins in NR are considered to originate branch points by hydrogen bonding.[15] As proof, the gel content in ordinary NR decreases with the enzymatic deproteinization of latex. However, it is clear that proteins have no direct effect on the green strength because DPNR shows almost the same green strength as that of NR before deproteinization.[16] Consequently, it seems reasonable to assume that the phospholipid groups in NR, which are presumed to be linked at the α terminal,[13,14] play an important role in developing the green strength.

In an attempt to gain greater understanding of the origin of the green properties characteristic of NR, we conducted a series of experiments on the relationship between the structure of NR and the green strength. In previous works,[17,17] we carried out the measurement of the green strength only for rubber film obtained by the solution-casting method. However, we found that the green strength of NR depends on the method used to prepare the test sheet, that is, casting from latex or a rubber solution or hot pressing of dry rubber. In general, the preparation of a film by the hot pressing of raw rubber is usually applied to prepare test sheets, as can be seen in ASTM D 6746-02. This standard method for preparing test sheets indicates that the sample will be pressed at 100°C for 5 min. However, this condition is not suitable for all rubbers because the viscosity and elasticity of rubbers depend on the chemical structure and molecular weight. Furthermore, no information has been given on the relationship

between the hot-pressing conditions and the green strength. Therefore, in this study, an attempt was made to show the variation of the green strength with changes in the preparation method of the testing film in connection with the structure of the branch points of NR versus that of IR. Here, the rubber film was prepared in three ways: casting from rubber latex, casting from a rubber solution in toluene, and hot pressing of dry rubber. The effects of the temperature and time of the hot-press treatment for the test film were also investigated to analyze the effect of the presumed branch points on the stress–strain behavior.

## EXPERIMENTAL

The preparation of NR films for the measurement of the stress–strain curve was carried out in three ways: (1) casting from rubber latex with a 30% dry rubber content and drying in an oven at 50°C for 24 h; (2) casting from a rubber solution [~3% (w/v)] in toluene including ~2% (w/v) ethanol and 1 phr butylated hydroxytoluene (BHT), keeping it at room temperature in the dark to evaporate the solvent, and eliminating the residual toluene with a vacuum oven at 40°C for 12 h; and (3) hot pressing of solid NR. Here, the rubber film from the hot-press method was made in two ways. First, the rubber film obtained by latex casting was pressed in a mold, which was sandwiched between two slide polyester films and pressed at 100–160°C for 10–40 min. After heating, the mold was cooled immediately to room temperature under pressure by a cooling system for 15 min. The resulting rubber film was subjected to the measurement of the stress–strain curve. Second, the rubber gum, sandwiched between two slide polyester films, was pressed in a mold at 100–160°C for 10–40 min. After the pressing, the mold was cooled immediately to room temperature under pressure for 15 min by a cooling system. To eliminate the residual molding strains, all the test sheets were stored at room temperature for 5 days before use.

### Rubber samples

Kraton IR-309 latex (Kraton Polymers LLC), provided by SRI R & D, Ltd. (Kobe, Japan), and NR latex, provided by Thai Rubber Latex Co. (Chonburi, Thailand), were used as IR and NR latices, respectively. NR in solution was prepared by the dissolution of the NR film obtained by latex casting in a toluene solution. NR gum was prepared by the coagulation of NR-latex with 5% (w/v) formic acid followed by washing and drying at 50°C for 24 h.
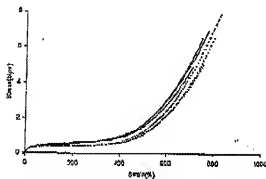
Figure 1 Stress-strain curves of three NR films obtained by (—) latex casting and (- - -) toluene solution casting.

## Measurement

The test pieces for the green strength measurement were stamped out with a type C dumbbell die according to ASTM D 412–87. The measurement was carried out with a tensile tester (Instron model 5569, Instron Co., PA) at room temperature. The testing crosshead speed of 500 mm/min was applied with a load cell of 100 N. The thickness of the sample was 0.5–1.5 mm. The measurement was repeated three to four times for each sample.

The molecular weight of the NR samples was determined by size exclusion chromatography (Jasco-Borwin, Tokyo, Japan) with two columns in series packed with a polystyrene-divinylbenzene copolymer gel having exclusion limits of $2.0 \times 10^7$ and $4 \times 10^9$. The rubber solution was prepared by the dissolution of rubber into tetrahydrofuran (LabScan, high-performance liquid chromatography grade) at a concentration of 0.05% (w/v) and filtered through a Millipore prefilter and 0.45-μm membrane filter (Alltech). Tetrahydrofuran was used as an eluent at a flow rate of 0.5 mL/min at $35 \pm 0.01°C$ with the refractive index as a detector. Standard IRs (Polymer Standard Service GmbH, Germany) were used for the calibration of the molecular weight.

## RESULTS AND DISCUSSION

Figure 1 shows the stress-strain curves of NR films prepared by latex-casting and solution-casting methods. Three to four test pieces were measured and plotted separately. The latex-casting film, represented by solid lines, showed higher modulus than the solution-casting film, represented by dotted lines, whereas the green strength and stress at break values of the two samples were almost the same (ca. 6.5 MPa). This value is in the range of green strength values reported previously.[6,11,17,18] The stress of the latex-casting film increased significantly at about 300% strain, whereas the stress of the solution-cast-

ing film increased significantly at about 400% strain. As reported previously,[19] the increase in the stress can be attributed to the crystallization of rubber chains on straining. Thus, the lower stress-strain behavior in the solution-casting film compared with that of the latex-casting film can be attributed to the lower crystallizability. It is reasonable to assume that the crystallization on stretching is related to the number of branch points per chain and chain entanglement. This assumption suggests that the branch points and/or chain entanglements of the NR film prepared by latex casting are higher than those of the NR film prepared by solution casting.

In a previous work, Kawahara et al.[16] studied the relationship between the green strength and gel content of rubber from NR latex during preservation in an ammonia solution. They found that the green strength of NR increased with the preservation time increasing, and this was due to the increase in the gel content. However, it was revealed that the deproteinization of the NR latex resulted in the disappearance of the gel fraction without a significant change in the green strength.[16] This finding clearly indicates that the gel content has no direct relationship with the green strength. We presumed that the long-chain branching in NR plays an important role in the high green strength in comparison with synthetic IR. Furthermore, we found that the solution-casting film of DPNR, which had no gel fraction, also showed a lower modulus than the DPNR latex-casting film, acting similarly to the NR film. The details of this work will be reported and discussed in the future.

In Figure 2, the stress-strain behavior of the NR film prepared by the hot-press method is compared with that of the NR films prepared by latex-casting and solution-casting methods; it is represented as the mean of three samples for each. Here, the hot-pressed films from latex casting and rubber gum
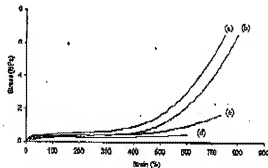


Figure 2 Stress-strain curves of NR sheets prepared by (a) latex casting, (b) toluene solution casting, (c) hot pressing of latex-casting film at 100°C for 15 min, and (d) hot pressing of rubber gum at 100°C for 15 min.

**TABLE I**
Molecular Weights of the Rubber Samples Obtained from Latex Casting, Toluene Solution Casting, and Hot Pressing at 100°C for 15 min

| Sample | Method | Weight-average molecular weight ($\times 10^6$) | Number-average molecular weight ($\times 10^5$) | Polydispersity |
|--------|--------|------|------|------|
| NR | Latex casting | 1.49 | 1.47 | 10.1 |
| NR | Solution casting | 1.42 | 1.27 | 11.2 |
| NR | Hot pressing | 1.53 | 1.43 | 10.7 |

were prepared by the pressing of rubber in the mold, which was sandwiched between two slides at 100°C for 15 min under high pressure. In the case of the NR pressed gum, the green strength was very low, and the strain at break was also very low versus that of the hot-pressed film from latex casting. This can be explained by the high elasticity of NR gum resulting in difficulty in preparing a homogeneous film, although this method has usually been used to prepare films for tensile testing. It is remarkable that the hot-press latex film showed very low green strength in comparison with the one without the hot-press treatment. This indicates that the stress–strain curve changes dramatically after the hot-press treatment of an NR latex film. Under the assumption that the branch points and entanglements affect the stress–strain behavior, the hot-press treatment of an NR latex film is presumed to bring about a structural change in the rubber chains by the treatment at a high temperature and a high pressure.

The molecular weights of the rubber samples prepared by various casting methods are almost the same, as shown in Table I. This indicates that the lower stress–strain curve of the NR film from toluene solution casting was not caused by the degradation of the rubber. The possibility of degradation after the hot-press treatment is also neglected because the samples from the latex-casting film showed almost the same molecular weights before and after the hot-press treatment. In previous works,[20,21] the role of the molecular weight in the

green strength of NR was studied. The results clearly showed a decrease in the green strength when the molecular weight of NR decreased by mastication.[20] In fact, not only the molecular weight but also the branch points were decomposed by mastication. Therefore, it is natural to consider the effect of the branch structure. It is known that NR from small rubber particles has a higher molecular weight than NR from large rubber particles.[22–24] However, NR from small rubber particles has shown very low green strength compared with that of NR from large rubber particles.[11] This behavior can be explained by the linear structure characteristics of NR from small rubber particles. Therefore, it can be deduced that the long-chain branching in NR is a dominant factor, affecting the high green strength of NR.

The effects of the temperature and time of the hot-press treatment were investigated to check the influence on the green strength and strain at break. The NR latex-cast film, which is comparable to NR gum, was used for this experiment to eliminate the effect of the inhomogeneity of rubber. To neglect the degradation of rubber at a high temperature during the hot-press treatment, an antioxidant, Wingstay-L, was added to the NR latex before casting in the latex form and before coagulation of the NR gum. Tables II and III show the green strength and strain at break of the NR latex-casting film and NR gum after hot-press treatment, respectively, at various conditions. The green strength and strain at break of the NR latex-casting film and NR gum showed no

**TABLE II**
Green Strength and Strain at Break of the NR Latex Casting Film After Hot-Press Treatments at Various Temperatures and Times

| | | NR latex casting film | | | |
|---|---|---|---|---|---|
| | | Without antioxidant | | With antioxidant | |
| Temperature (°C) | Time (min) | Green strength (MPa) | Strain at break (%) | Green strength (MPa) | Strain at break (%) |
| 100 | 10 | 1.36 ± 0.32 | 594 ± 64 | 1.08 ± 0.10 | 651 ± 46 |
| 100 | 20 | 1.50 ± 0.32 | 623 ± 48 | 1.07 ± 0.09 | 666 ± 41 |
| 100 | 30 | 1.11 ± 0.38 | 617 ± 75 | 0.89 ± 0.13 | 633 ± 37 |
| 100 | 40 | 1.41 ± 0.26 | 690 ± 51 | 1.08 ± 0.15 | 695 ± 27 |
| 120 | 10 | 1.57 ± 0.95 | 676 ± 22 | 1.02 ± 0.26 | 586 ± 61 |
| 140 | 10 | 1.15 ± 0.21 | 596 ± 68 | 0.85 ± 0.29 | 693 ± 62 |
| 160 | 10 | 0.71 ± 0.07 | 567 ± 67 | 0.48 ± 0.07 | 574 ± 95 |

**TABLE III**
Green Strength and Strain at Break of the NR Gum After Hot-Press Treatments at Various Temperatures and Times

| Temperature (°C) | Time (min) | NR gum | | | |
|---|---|---|---|---|---|
| | | Without antioxidant | | With antioxidant | |
| | | Green strength (MPa) | Strain at break (%) | Green strength (MPa) | Strain at break (%) |
| 100 | 10 | 0.36 ± 0.10 | 590 ± 78 | 0.63 ± 0.07 | 616 ± 60 |
| 100 | 20 | 0.61 ± 0.06 | 536 ± 31 | 0.55 ± 0.04 | 625 ± 64 |
| 100 | 30 | 0.57 ± 0.03 | 565 ± 53 | 0.50 ± 0.04 | 568 ± 49 |
| 100 | 40 | 0.54 ± 0.07 | 615 ± 39 | 0.51 ± 0.10 | 612 ± 94 |
| 120 | 10 | 0.49 ± 0.03 | 652 ± 86 | 0.44 ± 0.08 | 647 ± 78 |
| 140 | 10 | 0.55 ± 0.08 | 606 ± 42 | 0.39 ± 0.09 | 593 ± 65 |
| 160 | 10 | 0.31 ± 0.06 | 491 ± 117 | 0.26 ± 0.03 | 436 ± 115 |

significant changes after an increase in the time of the hot-press treatment at 100°C. This means that the decrease in the green strength after hot pressing is not related to the time of hot pressing in the range of 10–40 min. The increase in the temperature of the hot-press treatment resulted in a decrease in the green strength of the NR latex-casting film and NR gum. This was due to the fact that the high temperature caused oxidative degradation in NR. The addition of an antioxidant did not increase the green strength of the hot-pressed films prepared from the NR latex-casting film and NR gum, as shown in Tables II and III, respectively. Similar green strengths observed for the hot-pressed films with and without an antioxidant indicated that the oxidative degradation was not the main cause of the significant decrease in the green strength of the NR latex film after heat treatment. Furthermore, this assumption was confirmed by the decrease in the green strength without a change in the molecular weight of the NR latex-casting film after heat treatment at a low temperature (i.e., 100°C). We presumed that the very low green strength of the hot-pressed film was derived from the decrease in the crystallizability and/or entanglement because of the decrease in the branch points after heat treatment.

This assumption can be confirmed by the measurement of the stress–strain behavior for IR films prepared similarly to NR. As shown in Figure 3, the casting film from IR latex before and after the hot-press treatment showed very low stress–strain behavior, which was almost the same as that observed for the solution-casting film. This clearly indicates that the change in the stress–strain behavior of NR by the casting method and heat treatment is a phenomenon characteristic of NR.

Let us consider the difference in the structural purity of rubber chains: NR contains 100% cis-1,4-isoprene units, whereas Kraton IR-309 has been estimated to contain about 92% cis-1,4-isoprene units. As shown in Figure 4, $^1$H-NMR spectra of Kraton IR-309 exhibited small signals resonating at 1.60, 1.62, and 4.75 ppm, which were assigned to —$CH_3$ of trans-1,4-units, —$CH_3$ of 3,4-units, and =$CH_2$ of 3,4-units, respectively. The irregularity in the structure of Kraton IR-309 contributed to the lower crystallizability in comparison with NR. Accordingly, the fact that there was no difference in the stress–strain behavior in the latex-casting film of IR versus the solution-casting film and hot-pressed film can be attributed to the absence of crystallizability and low number of entanglements due to the lack of long-chain branching. If we consider
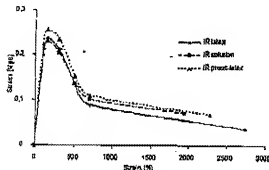


**Figure 3** Stress–strain curves of IR films prepared by (a) latex casting, (b) toluene solution casting, and (c) hot pressing of latex-casting film at 100°C for 15 min.
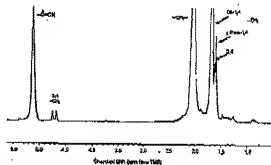


**Figure 4** $^1$H-NMR spectra of synthetic Kraton IR 309 (TMS = tetramethylsilane).

polymerization with an anionic initiator, Kraton IR-309 can be considered to be composed of almost linear rubber molecules, which also contribute to the very low green strength. This assumption is supported by the very low green strength of transesterified DPNR, which is comparable to that of IR.[17] Transesterified DPNR has been confirmed to be composed of linear molecules, in which almost all branch points are decomposed by a treatment with protease followed by a treatment with sodium methoxide. Both treatments result in the decomposition of branch points composed of proteins, lipids, and phospholipids.

It has been reported that the α-terminal group of a rubber chain in fresh NR latex consists of monophosphate and diphosphate groups linked with phospholipids.[13,19] The association or micelle formation of phospholipids is presumed to form long-chain branching, as illustrated in Figure 5. Here, the branch points are postulated to be derived from the micelle formation of phospholipids attached to the α-terminal group of a rubber chain. It is well known that phospholipids form a micelle in aqueous media. Rubber particles in latex have been reported to be covered by a bilayer composed of lipids in the inside and proteins on the outside.[20] The polar terminal groups in rubber molecules are assumed to be on the surface of rubber particles in latex, as illustrated in Figure 6. The α-terminal groups may associate together on the surface of rubber particles to form branch points. The branched structure of rubber points composed of phospholipids can form a reversed micelle in a toluene solution, which is

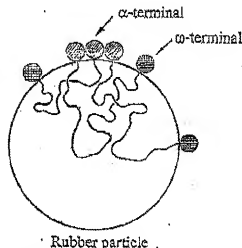Figure 5 Presumed structure of the branch points of rubber chains in the latex.

Figure 6 Presumed location of both terminal groups in the rubber particles.

expected to be less effective for the formation of branch points because of the concentration of rubber in the toluene solution. It is reasonable to think that the rubber film obtained by casting from a toluene solution shows lower stress-strain properties because of the reduction of long-chain branching. The high temperature and high pressure in the hot-pressing process will result in a conformational change in the long-chain fatty acid chains in phospholipids, leading to less effective formation between associated phospholipids at the branch points. This will result in a decrease in the number of long-chain branch points. Moreover, in this experiment, the rubber after hot pressing was cooled immediately under pressure. Therefore, the conformational change in the long-chain fatty acid was fixed and could not be rearranged to recover the original branch points. This behavior resulted in a decrease in the green strength of the rubber film from latex casting after hot pressing.

## CONCLUSIONS

The latex-casting film of NR showed the highest stress-strain behavior in comparison with the films produced by solution casting and by hot pressing, whereas synthetic IR showed similar stress-strain behavior independent of the preparation process of the testing films. This clearly indicates that the change in the stress-strain behavior with the casting method and heat treatment is a phenomenon characteristic of NR. It is remarkable that a mild heat treatment of the NR latex film at 100°C caused very low green strength without a change in the molecular
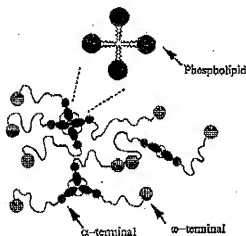
weight. These findings support the assumption that the branch points composed of mainly phospholipids decrease with the heat treatment of a latex-casting film and with casting from a toluene solution, and this will result in a decrease in the entanglement of rubber chains and crystallizability on stretching and contribute to the lower stress–strain behavior.

## References

1. Grechanovskii, V. A.; Ivanova, L. S.; Poddubnyi, I. Y. Rubber Chem Technol 1973, 46, 1234.
2. Blyler, L. L. Rubber Chem Technol 1969, 42, 823.
3. Grechanovskii, V. A.; Poddubnyi, I. Y.; Ivanova, L. S. Rubber Chem Technol 1974, 47, 342.
4. Hamed, G. R. Rubber Chem Technol 1981, 54, 576.
5. Gent, A. N. Trans Inst Rubber Ind 1954, 30, 139.
6. Eng, A. H.; Ejiri, S.; Kawahara, S.; Tanaka, Y. J Polym Sci Polym Symp 1994, 53, 5.
7. Nishiyama, N.; Kawahara, S.; Kakubo, T.; Eng, A. H.; Tanaka, Y. Rubber Chem Technol 1996, 69, 608.
8. Kawahara, S.; Nishiyama, N.; Kakubo, T.; Eng, A. H.; Tanaka, Y. Rubber Chem Technol 1996, 69, 600.
9. Kakubo, T.; Matsuura, A.; Kawahara, S.; Tanaka, Y. Rubber Chem Technol 1998, 71, 70.
10. Tanaka, Y.; Tadokoro, H. Polym J 1970, 1, 656.
11. Kawahara, S.; Kakubo, T.; Nishiyama, N.; Tanaka, Y.; Isono, Y.; Sakdapipanich, J. T. J Appl Polym Sci 2000, 78, 1510.
12. Sakdapipanich, J. T.; Suksujaretpom, S.; Tanaka, Y. J Rubber Res 1999, 2, 160.
13. Tarachiwin, L.; Sakdapipanich, J.; Ute, K.; Kitayama, T.; Bamba, T.; Fukusaki, E.; Kobayashi, A.; Tanaka, Y. Biomacromolecules 2005, 6, 1851.
14. Tarachiwin, L.; Sakdapipanich, J.; Ute, K.; Kitayama, T.; Tanaka, Y. Biomacromolecules 2005, 6, 1858.
15. Tanaka, Y.; Kawahara, S.; Tangpakdee, J. Kautsch. Gummi Kunstst 1997, 50, 6.
16. Kawahara, S.; Isono, Y.; Sakdapipanich, J. T.; Tanaka, Y.; Eng, A. H. Rubber Chem Technol 2002, 75, 739.
17. Kawahara, S.; Isono, Y.; Kakubo, T.; Tanaka, Y.; Eng, A. H. Rubber Chem Technol 2000, 73, 39.
18. Kawahara, S.; Isono, Y.; Sakdapipanich, J. T.; Tanaka, Y.; Eng, A. H. Rubber Chem Technol 2002, 75, 739.
19. Mark, J. E. Polym Eng Sci 1979, 19, 254.
20. Forbez, W. G.; MacLeod, L. A. Trans IRI 1958, 30, 154.
21. Hamed, G. R. Rubber Chem Technol 1981, 54, 576.
22. Subramaniam, A. RRIM Technol Bul 1980, 4, 20.
23. Yeang, H. Y.; Esah, Y.; Samsidaan, H. J. Nat Rubber Res 1995, 10, 108.
24. Tarachiwin, L.; Sakdapipanich, J.; Tanaka, Y. Rubber Chem Technol 2005, 78, 694.
25. Wren, W. G. Rubber Chem Technol 1942, 15, 107.

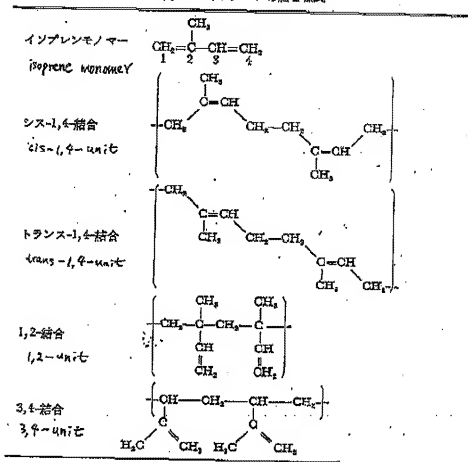# イソプレンゴム

小室経治　上田明男　著
和久哲夫　和田亮郎

害では除外する。

表 2-1 イソプレンの結合様式



表 2-2 イソプレンゴムのミクロ構造

| 結 合 様 式 | | 天然ゴム | 合成イソプレンゴム | |
|---|---|---|---|---|
| | | | チーグラー一触媒 | リチウム触媒 |
| ミクロ構造 (%) | シス-1,4 | 98< | 97 | 92 |
| | トランス-1,4 | — | — | 2 |
| | 1,2 結合 | — | — | — |
| | 3,4 結合 | 2> | 3 | 6 |

小 鷲 經 治　　昭和28年　横浜ゴム㈱入社
　　　　　　　　昭和34年　日本ゼオン㈱入社
　　　　　　　　現　在　日本ゼオン㈱
　　　　　　　　　　　　　ゴム開発センター主管

上 田 明 男　　昭和37年　日本ゼオン㈱入社
　　　　　　　　現　在　日本ゼオン㈱
　　　　　　　　　　　　　ゴム開発センター主任研究員

和 田 克 郎　　昭和36年　日本ゼオン㈱入社
　　　　　　　　現　在　日本ゼオン㈱
　　　　　　　　　　　　　ゴム開発センター主任研究員

和 久 哲 夫　　昭和42年　日本ゼオン㈱入社
　　　　　　　　現　在　日本ゼオン㈱
　　　　　　　　　　　　　ゴム開発センター研究員

(Cover page)

Treatise of technologies for processing synthetic rubbers, Vol.1

Isoprene Rubbers

Written by Keiji KOMURO, Akio UEDA, Yoshio WADA, and Tetsuo WAKU
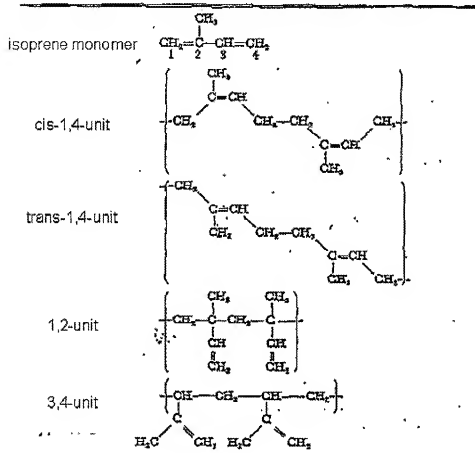
## Table 2-1 Bonding modes of isoprene



| | |
|---|---|
| isoprene monomer | CH₂=C—CH=CH₂ structure |
| cis-1,4-unit | |
| trans-1,4-unit | |
| 1,2-unit | |
| 3,4-unit | |

## Table 2-2 Micro structures of isoprene rubbers

| Bonding mode | | Natural rubber | Synthetic isoprene rubber | |
|---|---|---|---|---|
| | | | Ziegler catalyst | Lithium catalyst |
| Micro structure (%) | cis-1,4-unit | 98< | 97 | 92 |
| | trans-1,4-unit | — | — | 2 |
| | 1,2-unit | — | — | — |
| | 1,3-unit | 2> | 3 | 6 |